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**UNIVERSITY OF TORONTO
STUDIES**

**PAPERS FROM THE CHEMICAL
LABORATORIES**

**No. 69: A NEW TYPE OF CATALYSIS, THE ACCELERATION
BY CHROMIC ACID OF THE REACTION BETWEEN
BROMIC AND HYDRIODIC ACID, BY ROBERT H. CLARK.**

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A NEW TYPE OF CATALYSIS. THE ACCELERATION BY CHROMIC ACID OF THE REACTION BETWEEN BROMIC AND HYDRIODIC ACIDS

BY ROBERT H. CLARK

The catalytic action of chromic acid on the rate of oxidation of hydrogen iodide by bromic acid was discovered by Ostwald in the course of his "Studien zur chemischen Dynamik;"¹ and when my own work had cleared up the kinetics of the reaction in question,² I entered on a detailed investigation of this case of catalysis, which has yielded some very remarkable results.

The method of carrying out the measurements, the stock solutions, and the units employed in recording the results, are all as described in my previous paper, with the addition of a solution of potassium bichromate, 0.1667-F, and another 0.001251-F, which were standardized against the acid by means of a solution of caustic potash and phenolphthalein. In the tables the number of cubic centimeters of 0.00125-F bichromate³ is given under *Cr*.

As in the reaction between bromic and hydriodic acids, the presence of air had no material effect on the results of the measurements; and small quantities of iodine, such as are liberated during the reaction, exerted little or no effect on the rates.

EFFECT OF THE BICHROMATE ON THE RATE

The fact that the increased liberation of iodine in presence of chromic acid is not accompanied by a proportional reduction of the latter was observed by Ostwald, who found also that the increase in rate is proportional to the concentration of the chromic acid. Both these conclusions are supported by the measurements of Table I. In the first place, the

¹ Zeit. phys. Chem., 2, 138 (1888).

² Jour. Phys. Chem., 10, 679 (1906).

³ 0.00125 gram-formula-weights $K_2Cr_2O_7$ per liter.

TABLE I
KBrO₃, 20.5; KI, 98.67; HCl, 95.15; Vol., 250 cc; Temp., 30° C.

<i>t</i>	Cr	<i>x</i>	<i>x'</i>	<i>R</i> ₀	Ac/Cr	<i>t</i>	Cr	<i>x</i>	<i>x'</i>	<i>R</i> ₀	Ac/Cr
5	0	0.19	0.19	0.038	—	10	0	0.38	0.385	0.038	—
5	2	0.35	0.354	0.071	0.017	10	2	0.70	0.71	0.071	0.016
5	4	0.50	0.505	0.10	0.015	10	4	0.95	0.97	0.097	0.015
5	6	0.65	0.659	0.13	0.015	10	6	1.25	1.28	0.13	0.015
5	10	0.97	0.98	0.20	0.016	10	10	1.92	1.99	0.20	0.016
5	12	1.17	1.20	0.24	0.017	10	12	2.30	2.40	0.24	0.017
5	14	1.29	1.33	0.27	0.016	10	14	2.55	2.67	0.27	0.018
5	16	1.48	1.52	0.30	0.016	10	16	2.90	3.14	0.31	0.017
5	18	1.54	1.70	0.34	0.017	10	18	3.22	3.39	0.34	0.016
5	20	1.83	1.89	0.38	0.017	10	20	3.55	3.77	0.38	0.017

values of *x'* for *t* = 10 are just double those for *t* = 5, therefore no perceptible diminution in the concentration of the bichromate (reduction) can have occurred in the interval. In the second, the rate of liberation of iodine (*R*₀) is not proportional to the concentration of bichromate, but the acceleration:

$$Ac = R_0 - R_0(Cr = 0)$$

is; this is shown by the constancy of the quotient *Ac/Cp*, and graphically in Fig 1. The experiments of Table II, more-

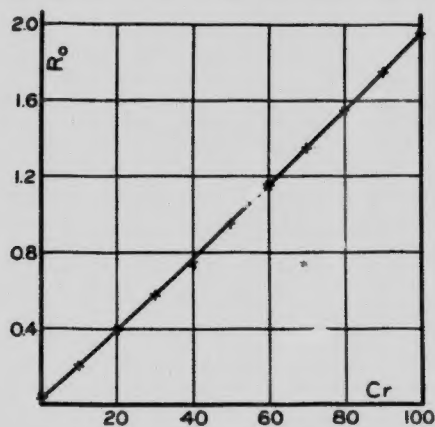


Fig. 1

TABLE II

KBrO₃, 20.5; KI, 98.67; HCl, 95.15; Cr, 2.0; Vol., 250 cc;
Temp., 30° C.

<i>t</i>	<i>x</i>	<i>x'</i>	<i>R</i> ₀
240	13.95, 14.07, average 14.01	19.83	0.083
300	16.33, 16.33, " 16.33	24.65	0.082
$\frac{24.65 - 19.83}{300 - 240} = 0.080$			

over, show that even after the reaction had proceeded for four hours during which the additional iodine liberated because of the presence of the bichromate was oxidimetrically equivalent to 56 percent of the latter, there was no diminution in the rate of liberation of iodine except that due to the fall in the concentrations of the bromate, iodide and acid, which was allowed for in computing *R*₀.

EFFECT OF THE CONCENTRATIONS OF BROMATE, IODIDE AND ACID ON THE RATE

Systematic measurements were undertaken to ascertain the effect of changes in the concentration of each of the reagents in turn, on the rate of liberation of iodine. The results, which are contained in Tables III-VI, show that the rate is

TABLE III

KBrO₃, 20.5; KI, 98.67; HCl, 95.15; Vol., 250 cc; Temp., 30° C.;
t = 5

Cr	<i>x</i>	<i>x'</i>	<i>R</i> ₀	Cr	<i>x</i>	<i>x'</i>	<i>R</i> ₀
0	0.19	0.19	0.038	18	1.64	1.70	0.34
1	0.25	0.253	0.05	20	1.83	1.89	0.38
2	0.35	0.354	0.07	30	2.70	2.83	0.57
3	0.40	0.404	0.08	40	3.50	3.71	0.74
4	0.50	0.505	0.10	50	4.35	4.69	0.94
6	0.65	0.659	0.13	60	5.25	5.74	1.15
8	0.81	0.82	0.16	70	6.07	6.73	1.35
10	0.97	0.98	0.20	80	6.95	7.82	1.56
12	1.17	1.20	0.24	90	7.65	8.71	1.74
14	1.29	1.33	0.27	100	8.35	9.73	1.95
16	1.48	1.52	0.30				

TABLE IV

KBrO₃, 20.5 × *f*; KI, 98.67; HCl, 95.15; Vol., 250 cc; Temp., 30°C

<i>t</i>	Cr	<i>f</i>	<i>x</i>	<i>x'</i>	R ₀
5	10	2	2.00	2.07	0.41
5	12	2	2.33	2.42	0.48
5	14	2	2.60	2.71	0.54
5	16	2	2.95	3.10	0.62
5	18	2	3.27	3.45	0.69
5	20	2	3.57	3.78	0.76
5	6	3	2.01	2.02	0.40
5	10	3	2.87	3.01	0.60
5	14	3	3.82	4.06	0.81
10	18	2	6.30	7.01	0.70
10	20	2	6.80	7.61	0.76

TABLE V

KBrO₃, 20.5; KI, 98.67 × *f*; HCl, 95.15; Vol., 250 cc; Temp., 30°C

<i>t</i>	Cr	<i>f</i>	<i>x</i>	<i>x'</i>	R ₀
5	10	2	2.00	2.07	0.41
5	12	2	2.32	2.41	0.48
5	14	2	2.58	2.68	0.54
5	16	2	2.94	3.06	0.61
5	18	2	3.24	3.40	0.68
5	20	2	3.58	3.77	0.76
5	6	3	2.00	2.01	0.40
5	10	3	2.87	2.99	0.60
5	14	3	3.80	4.00	0.80
10	16	2	5.70	6.23	0.62
10	18	2	6.30	6.93	0.69
10	20	2	6.79	7.52	0.75

TABLE VI

KBrO₃, 20.5; KI, 98.67; HCl, 95.15 × 2; Vol., 250 cc; Temp., 30° C; $t = 5$

Cr	x	x'	n , 1st appx.	n , 2nd appx.	R_0
0	0.90	0.91	2.00	2.00	0.18
2	1.17	1.19	1.72	1.73	0.24
4	1.48	1.51	1.58	1.58	0.30
6	1.86	1.91	1.52	1.53	0.38
8	2.22	2.30	1.45	1.49	0.46
10	2.58	2.68	1.41	1.44	0.54
12	2.97	3.10	1.35	1.37	0.62
14	3.27	3.42	1.34	1.36	0.68
16	3.61	3.83	1.29	1.32	0.77
18	3.96	4.21	1.27	1.30	0.84
20	4.30	4.60	1.23	1.28	0.92
30	6.05	6.63	1.16	1.22	1.33
40	7.44	8.32	1.09	1.13	1.66
50	9.00	10.30	1.03	1.12	2.06
60	10.30	12.04	0.97	1.07	2.41
70	11.50	14.17	0.93	1.05	2.83
80	12.95	15.71	0.90	1.01	3.14
90	14.19	17.63	0.89	1.01	3.53
100	15.22	19.24	0.87	0.96	3.85

proportional to the concentration of the bromate and to that of the iodide (the same as in absence of chromate); but that the effect produced by changing the concentration of the acid depends on the amount of bichromate present.

The experiments of Table III serve as standard for comparison, while in the other three the concentrations of bromate, iodide and acid respectively were multiplied by the variable factor f . Under R_0 in the last column is entered the "initial rate"

$$R_0 = dx/dt(x=0) = x'/t$$

that is, the number of cubic centimeters of hundredth-normal iodine liberated per minute in a solution of the composition indicated at the head of the table.

Method of computing x' and n

The general differential equation connecting the rate of

liberation of iodine with the concentrations of the reagents may therefore be written:

$$dx/dt = K(A-x)(B-x)(C-x)^n(1+M.Cr) \quad (1)$$

where A , B and C are the concentrations of the bromate, iodide and acid respectively, and n depends on the concentration of the bichromate; K and M are constants.

By comparing the iodine readings (x) from Tables III and VI, in the latter of which the concentration of the acid was double that in the former, a first approximation to the values of n was obtained:

$$n \text{ first approx.} = \frac{\log x (\text{Table VI}) - \log x (\text{Table III})}{\log 2} \quad (2)$$

The values so computed are entered in Table VI under " n first approx." These approximate values were then introduced into Equation (1), which was integrated by series, and used to obtain a first approximation to the values of x' for Table VI.

$$x' = KABC^n(1+M.Cr) = x + (1/2A + 1/2B + n/2C)x^2 + 1/3A^2 + 1/3B^2 + n^2 + n/6C^2 + 1/3AB + n/3AC + n/3BC)x^3 \quad (3)$$

A second approximation to the true value of n was then made, using x' (Equation 3) in place of x in Equation (2); the numbers so obtained are entered under " n second approx" in Table VI. Fig. 2 shows these values of n plotted as a

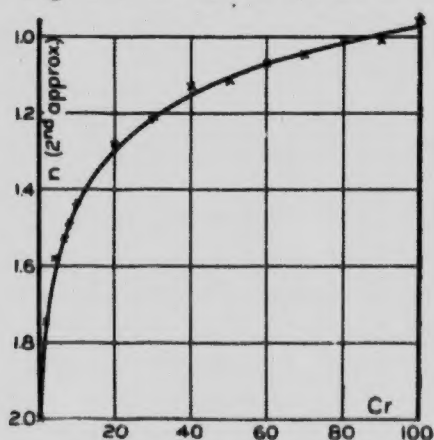


Fig. 2

function of Cr . When $Cr = 0$, the rate is proportional to the second power of the concentration of the acid; on addition of potassium bichromate the power diminishes until $Cr = 80$, when the rate is proportional to the first power of the concentration of the acid, and the curve (Fig. 2) becomes a straight line.

In Ostwald's "Lehrbuch der Allgemeinen Chemie" II (2), p 262, that author says: "So long as the catalyser is neither altered, formed, nor destroyed by the reagents or products of the reaction, its influence is exerted only on the value of the velocity constant, and not on the character of the kinetic equation." The present case is evidently an exception.

INTERPRETATION OF THE RESULTS

These results may be expressed by assuming that:

(i) In solutions containing bromate, bichromate acid and iodide, two reactions take place simultaneously, both resulting in the liberation of iodine.

(ii) The rate of the first reaction is proportional to the concentrations of the bromate, and iodide and to the square of that of the acid; while that of the second is proportional to the concentrations of bromate, iodide and acid, and slightly less than proportional to that of the bichromate.

(iii) The second reaction takes place without proportional reduction of the bichromate.

The corresponding kinetic differential equations are:

$$\frac{\partial x}{\partial t} = K_1(A-x)(B-x)(C-x)^2, \text{ and}$$

$$\frac{\partial x}{\partial t} = K_2(A-x)(B-x)(C-x)Cr$$

and the rate at which iodine is liberated in the solution:

$$dx/dt = (A-x)(B-x)(C-x)(K_1C-x + K_2Cr) \quad (4)$$

The values of the two constants in this equation were calculated from the two experiments of Table VI in which $Cr = 0$ and $Cr = 100$ respectively; they are, $K_1 = 645 \times 10^{-12}$ and $K_2 = 333 \times 10^{-10}$. The change of n with the concentration of the bichromate (Table VI and Fig. 2) is in quantitative accord with these assumptions, as may be seen by

comparing the values of "*n second approx*" in Table VI with those calculated from the equation:¹

$$n_{calc.} = \frac{\log(2K_1C + K_1Cr) - \log(K_1C + K_2Cr)}{\log 2} + 1 \quad (5)$$

TEMPERATURE COEFFICIENT

In order to find the temperature coefficients of the rates involved, I repeated the experiments of Table IV at zero. (See Table VII.)

TABLE VII

Cr	<i>n</i> , 2d appx.	<i>n</i> calc.	Cr	<i>n</i> , 2d appx.	<i>n</i> calc.
0	2.00	2.00	20	1.28	1.26
2	1.73	1.75	30	1.22	1.19
4	1.58	1.62	40	1.13	1.12
6	1.53	1.53	50	1.12	1.11
8	1.49	1.47	60	1.07	1.10
10	1.44	1.41	70	1.05	1.09
12	1.37	1.37	80	1.01	1.07
14	1.36	1.34	90	1.01	1.06
16	1.32	1.30	100	0.96	1.04
18	1.30	1.28			

Under "coeff" is entered the temperature coefficient, that is the cube root of the ratio of the two rates R_0 at 30° and at 0°. The coefficient varies with the amount of bichromate present, as is shown graphically in Fig. 3; the similarity between this curve and that of Fig. 2 furnishes another argument in support of the assumption of two simultaneous reactions. The coefficient falls off gradually as the quantity of bichromate increases until $Cr = 60$, when it becomes constant at 1.19; this may be taken as the temperature coefficient.

¹ In Table VI the concentration of the acid was twice that in Table III; hence, comparing values of R_0 from experiments in which the concentration of bichromate was the same,

$$\text{by Equation (1)} \quad \frac{R_0(\text{Table VI})}{R_0(\text{Table III})} = 2^n$$

$$\text{by Equation (4)} \quad \frac{R_0(\text{Table VI})}{R_0(\text{Table III})} = \frac{2(2K_1C + K_2Cr)}{K_1C + K_2Cr}$$

Equation 5 is obtained by equating these two expressions and taking the logarithms; C refers to the acid of Table III.

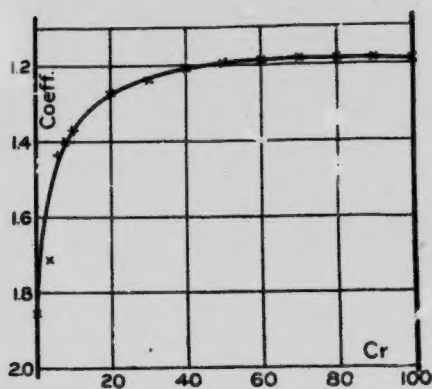


Fig. 3

cient of the second reaction of page 350, while that of the first is 1.85.

TABLE VIII

KBrO₃, 20.5; KI, 98.67; HCl, 190.3; Vol., 250 cc; Temp., 0° C;
 $t = 5$

Cr	x	x'	R_0	Coeff.
0	—	—	—	1.85 ¹
4	0.30	0.30	0.56	1.71
6	0.63	0.63	0.13	1.43
8	0.85	0.87	0.17	1.40
10	1.05	1.07	0.21	1.37
12	1.25	1.27	0.25	1.35
14	1.42	1.45	0.29	1.33
16	1.76	1.80	0.36	1.29
18	1.91	1.95	0.39	1.29
20	2.10	2.16	0.43	1.28
30	3.29	3.45	0.69	1.24
40	4.45	4.75	0.95	1.21
50	5.45	5.91	1.18	1.20
60	6.45	7.09	1.42	1.19
70	7.25	8.08	1.62	1.19
80	8.15	9.18	1.84	1.19
90	9.00	10.28	2.06	1.19
100	9.72	11.24	2.25	1.19

¹ This Journal, 10, 679 (1906).

CHROMIC ACID AND THE ANALOGOUS REACTIONS

The difficulty of inventing any hypothetical mechanism to explain the part played by the bichromate is enhanced by the circumstance that this case stands alone. Mr. Dushman¹ has shown that potassium bichromate is without action on the rate of the reaction between iodic and hydriodic acids; and by means of a few measurements I have ascertained that the rates of the reactions between

Iodic and hydrobromic acids
Bromic and hydrobromic acids
Chloric and hydrobromic acids and
Chloric and hydriodic acids

are likewise uninfluenced by the presence of potassium bichromate.

Summary

(1) Addition of potassium bichromate to a solution containing bromic and hydriodic acids brings a new reaction into operation, which consists in the liberation of iodine at a rate proportional to the concentrations of the bromate, iodide, bichromate and acid, without reduction of the bichromate. The normal reaction, whose rate is proportional to the concentration of the bromate and iodide and to the square of that of the acid, goes on unaffected by the presence of the bichromate.

(2) The processes of oxidation of hydriodic and hydrobromic acids by the oxyacids of the halogens, other than that of hydriodic by bromic acid, are not affected by the presence of potassium bichromate. Although in other respects the members of this group of reactions resemble one another closely from the kinetic point of view as well as from that of pure chemistry, the analogy fails at this point.

In both respects this case of catalysis is unique.

I desire to express my thanks to Prof. W. Lash Miller, under whose direction these measurements were carried out in the winter of 1904-5.

¹ Jour. Phys. Chem., 8, 453 (1904).
The University of Toronto
February, 1907

